- 41. A process according to Claim 39, wherein said starting reaction medium is heated to a temperature of at least 120°C.
- 42. A process according to Claim 39, wherein said reaction medium is heated along a decreasing temperature gradient.
- 43. A process according to Claim 39, wherein the heating time is at least 5 minutes, and not more than 24 hours.
- 44. A process according to Claim 39, wherein the heating time is at least 30 minutes, and not more than 5 hours.
- 45. A process according to Claim 39, wherein at the end of the dimerization reaction, the starting monomer is removed.
- 46. A process according to Claim 39, wherein at the end of the dimerization reaction, the starting monomer is removed by distillation.
- 47. A process according to Claim 39 for the continuous preparation of a composition containing at least one isocyanate dimer containing a uretidinedione unit, wherein after the dimerization reaction, the unreacted monomers are removed and are recycled into the dimerization step.

A process for the preparation of a low-viscosity polyfunctional isocyanate composition containing at least one isocyanate trimer containing an isocyanurate and/or biuret unit and at least one isocyanate dimer containing a uretiainedione unit, from starting isocyanate monomers, in which the isocyanate groups are borne by sp³ carbon atoms, and optionally from other monomers, this process comprising the following steps:

Cub 32

- heating the starting reaction medium, in the absence of dimerization catalyst, to a temperature of at least 80°C, and of not more than 200°C, for a period of less than 24 hours;
- ii) reacting the reaction product from step i) containing unreacted monomers with a (cyclo)condensation catalyst, under (cyclo)trimerization conditions;
- iii) removing the unreacted starting monomers from the reaction product from step ii);
- iv) isolating the low-viscosity polyfunctional isocyanate composition comprising at least one isocyanate trimer and at least one isocyanate dimer.

A process for the preparation of a low-viscosity polyfunctional isocyanate composition containing at least one isocyanate trimer containing an isocyanurate and/or biuret unit and at least one isocyanate dimer containing a uretidinedione unit, from starting isocyanate monomers, in which the isocyanate groups are borne by sp³ carbon atoms, and optionally from other monomers, this process comprising the following steps:

- i) heating the starting reaction medium, in the absence of dimerization catalyst, to a temperature of at least 120°C, and of not more than 170°C, for a period of less than 5 hours;
- ii) reacting the reaction product from step i) containing unreacted monomers with a (cyclo)condensation catalyst, under (cyclo)trimerization conditions;
- iii) removing the unreacted starting monomers from the reaction product from step ii);

iv) isolating the low-viscosity polyfunctional isocyanate composition comprising at least one isocyanate trimer and at least one isocyanate dimer.

A process for the preparation of a low-viscosity polyfunctional isocyanate composition containing at least one isocyanate trimer containing an isocyanurate and/or biuret unit and at least one isocyanate dimer containing a uretidinedione unit, from starting isocyanate monomers in which the isocyanate groups are borne by sp³ carbon atoms, and optionally from other monomers, this process comprising the following steps:

- i) reacting the starting monomers with a (cyclo)trimerization or (cyclo) condensation catalyst under (cyclo)trimerization or (cyclo)condensation conditions;
- ii) heating the reaction product from step i) containing unreacted isocyanate monomers, in the absence of dimerization catalyst, to a temperature of at least 80°C, and of not more than 200°C, for a period of less than 24 hours;
- iii) removing the unreacted starting monomers from the reaction product from step ii);
- iv) isolating the low-viscosity polyfunctional isocyanate composition comprising at least one isocyanate trimer and at least one isocyanate dimer.
- A process for the preparation of a low-viscosity polyfunctional isocyanate composition containing at least one isocyanate trimer containing an isocyanurate and/or biuret unit and at least one isocyanate dimer containing a uretidinedione unit, from starting isocyanate monomers in which the isocyanate groups are borne by sp³ carbon atoms, and optionally from other monomers, this process comprising the following steps:

- i) reacting the starting monomers with a (cyclo)trimerization or (cyclo) condensation catalyst under (cyclo)trimerization or (cyclo)condensation conditions;
- heating the reaction product from step i) containing unreacted isocyanate monomers, in the absence of dimerization catalyst, to a temperature of at least 120°C, and of not more than 170°C, for a period of less than 5 hours;
- iii) removing the unreacted starting monomers from the reaction product from step ii);
- iv) isolating the low-viscosity polyfunctional isocyanate composition comprising at least one isocyanate trimer and at least one isocyanate dimer.
- A process for the preparation of a low-viscosity polyfunctional isocyanate composition comprising at least one isocyanate dimer containing a uretidinedione unit and at least one other compound having a function derived from the isocyanate function, from starting isocyanate monomers in which the isocyanate groups are borne by sp³ carbon atoms and another compound comprising at least one function other than isocyanate, which is reactive with the isocyanate function, this process comprising the following steps:
- i) heating the starting reaction medium, in the absence of dimerization catalyst, to a temperature of greater than at least 80°C, and less than at least 200°C, for a period of less than 24 hours;
- ii) reacting together the reaction product from step i) containing unreacted isocyanate monomers and a compound comprising at least one function other than the isocyanate function, which is reactive with the isocyanate function, optionally in the presence of a catalyst;

- removing from the reaction product from step ii) the isocyanate monomers and, where appropriate, the compound comprising at least one function other than the isocyanate function, which is reactive with the isocyanate function;
- iv) isolating the polyfunctional isocyanate composition of low-viscosity comprising at least one isocyanate dimer containing a uretidinedione unit and at least one other function derived from the isocyanate function.
- A process for the preparation of a low-viscosity polyisocyanate composition comprising at least one isocyanate dimer containing a uretidinedione unit and at least one other compound containing a function derived from the isocyanate function, starting with isocyanate monomers in which the isocyanate groups are borne by sp³ carbon atoms and with another compound comprising at least one function other than isocyanate, which is reactive with the isocyanate function, this process comprising the following steps:
- (i) reacting an isocyanate monomer with a compound comprising at least one function other than an isocyanate function, which is reactive with the isocyanate function, optionally in the presence of a catalyst;
- heating the reaction mixture from step i) containing unreacted isocyanate monomers, in the absence of dimerization catalyst, to a temperature of greater than at least 80° C, and not more than 200° C, for a period of less than 24 hours ;
- iii) removing from the reaction product from step ii) the monomers and, where appropriate, the compound comprising at least one function other than the isocyanate function, which is reactive with the isocyanate function;

iv) isolating the low-viscosity polyisocyanate composition comprising at least one polyisocyanate trimer and at least one polyisocyanate dimer.

process for the preparation of a low-viscosity polyfunctional isocyanate composition comprising at least one isocyanate dimer containing a uretidinedione unit and at least one other compound having a function derived from the isocyanate function, from starting isocyanate monomers in which the isocyanate groups are borne by sp³ carbon atoms and another compound comprising at least one function other than isocyanate, which is reactive with the isocyanate function, this process comprising the following steps:

- i) reacting an isocyanate monomer with a compound comprising at least one function other than an isocyanate function, which is reactive with the isocyanate function, optionally in the presence of a catalyst;
- ii) heating the reaction mixture from step i) containing unreacted isocyanate monomers, in the absence of dimerization catalyst, to a temperature of greater than at least 120°C, and not more than 170°C, for a period of less than 5 hours;
- iii) removing from the reaction product from step ii) the monomers and, where appropriate, the compound comprising at least one function other than the isocyanate function, which is reactive with the isocyanate function;
- iv) isolating the low-viscosity polyisocyanate composition comprising at least one polyisocyanate trimer and at least one polyisocyanate dimer.
- 55. A process according to Claim 48, wherein said isocyanate dimer is obtained by heating the reaction medium along a decreasing temperature gradient.

- 56. A process according to Claim 52, wherein said function derived from the isocyanate function is a carbamate, allophanate, urea, biuret and/or blocked isocyanate function.
- 57. A process according to Claim 52, for the preparation of a low-viscosity polyfunctional isocyanate composition comprising at least one uretidinedione isocyanate dimer, and at least one compound having a biuret function, comprising the reaction, in step ii), of isocyanate monomers with water.
- 58. A process according to Claim 53 for the preparation of a low-viscosity polyfunctional isocyanate composition comprising at least one uretidinedione isocyanate dimer, and at least one compound having a biuret function, comprising the reaction, in step i), of isocyanate monomers with water.
- A process for the preparation of a low-viscosity (poly)isocyanate composition comprising at least one isocyanate dimer containing a uretidinedione unit, from starting isocyanate monomers in which the isocyanate groups are borne by sp³ carbon atoms, comprising the step of heating a starting reaction medium comprising said isocyanates monomeres, in the absence of a dimerization catalyst, to a temperature of at least 50°C and of not more than 200°C for a period of not more than 24 hours, comprising adding to the reaction medium containing the starting monomers a compound of general formula I:

$$R = C - (CH_2OH)_3$$
n
(I)

in which

which the hydrocarbon-based chain can be interrupted by one or more chalcogen atoms and can bear 1 to 3 OH groups, and n is an integer ranging from 1 to 3, and/or products derived from this derivative by a reaction with a compound bearing an aliphatic isocyanate function.

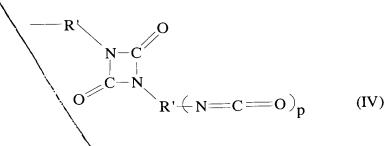
60. A process for the preparation of a low-viscosity (poly)isocyanate composition comprising at least one isocyanate dimer containing a uretidinedione unit, from starting isocyanate monomers in which the isocyanate groups are borne by sp³ carbon atoms, comprising the step of heating a starting reaction medium comprising said isocyanates monomeres, in the absence of a dimerization catalyst, to a temperature of at least 50°C and of not more than 200°C for a period of not more than 24 hours comprising adding to the reaction medium containing the starting monomers a compound of general formula II and/or III below:

$$R_1$$
 $CH_2OCONHX_1$
 $CH_2OCONHX_3$
 R_1
 $CH_2OCONHX_3$
 R_2
 $CH_2OCONX'X"_1$
 $CH_2OCONX'_2X"_2$
 $CH_2OCONX'_3X"_3$
 R_1
 $CH_2OCONX'_3X"_3$
 R_2
 $CH_2OCONX'_3X"_3$
 R_3
 R_4
 $CH_2OCONX'_3X"_3$

in which

one or more of X_1 , X_2 and X_3 represents a group R'-(N=C=O)_p in which R' is a p-valent aliphanic group and p is an integer ranging from 0 to 5,

the others representing, where appropriate, a group of formula



R' and p being as defined above,

 R_1 is R, with the OH groups substituted, where appropriate, with a group CONX $_1$ H, X_1 being as defined above, at least one of NX' $_1$ X'' $_1$, NX' $_2$ X'' $_2$ and NX' $_3$ X'' $_3$ represents the group

$$\begin{array}{c}
R' - (N = C = O)_p \\
C - NH - R' - (N = C = O)_p \\
0
\end{array}$$
(V)

R' and p being as defined above, the others representing a group NX_1H or NX_1 -silyl with X_1 as defined above and R_2 being R, with the OH groups substituted, where appropriate, with a group $CONX_1H$, or

$$-CO - N - R' - (N = C = O)_{p}$$

$$C - NH - R' - (N = C = O)_{p}$$

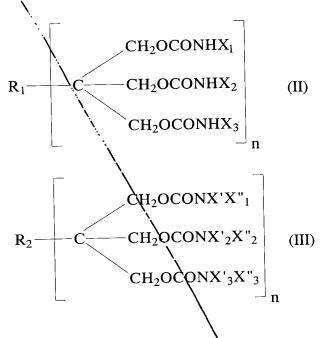
$$VI)$$

$$O$$

$$-10 -$$

R' and p being as defined above, and n is an integer ranging from 1 to 3.

- A process according to Claim 59, wherein R is a C_1 - C_4 alkyl group substituted with 1 to 3 OH groups.
- 62. A process according to Claim 59, wherein said compound of general formula I is selected from pentaerythritol and trimethylolpropane, and the compounds of general formulae II and IM are selected, where appropriate, from the corresponding pentaerythritol and trimethylolpropane derivatives of general formula II and/or III below:



in which

one or more of X_1 , X_2 and X_3 represents a group R' - $(N=C=O)_p$ in which R' is a p-valent aliphatic group and p is an integer ranging from 0 to 5, the others representing, where appropriate, a group of formula

R' and p being as defined above,

 R_1 is R, with the OH groups substituted, where appropriate, with a group CONX $_1H$, X_1 being as defined above, at least one of NX' $_1X''_1$, NX' $_2X''_2$ and NX' $_3X''_3$ represents the group

$$\begin{array}{c}
R' - (N = C = O)_p \\
C - NH - R' - (N = C = O)_p \\
\parallel & (V)
\end{array}$$

R' and p being as defined above, the others representing a group NX_1H or NX_1 -silyl with X_1 as defined above and R_2 being R, with the OH groups substituted, where appropriate, with a group $CONX_1H$, or

$$-CO - N - R' - (N - C - O)_{p}$$

$$C - NH - R' - (N - C - O)_{p}$$

$$O$$

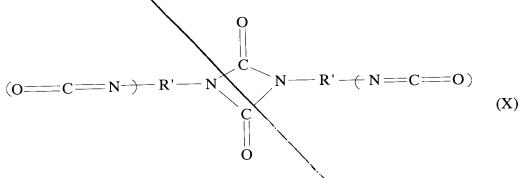
$$(VI)$$

R' and p being as defined above,

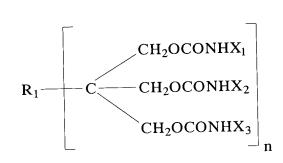
and n is an integer ranging from 1 to 3,

wherein R₁ and/or R₂ represents a group selected from CH₂0H and CH₃CH₂.

- 63. A process according to Claim 39, wherein said starting isocyanate monomers are diisocyanates selected from the group consisting of hexamethylene diisocyanate, tetramethylene diisocyanate, norbornane dimethylene diisocyanate, isophorone diisocyanate, bis(isocyanato)cyclohexylmethane and 2-methylpentamethylene diisocyanate.
- A low-viscosity polyfunctional isocyanate composition comprising at least one ureticinedione isocyanate dimer and at least one compound having a biuret function, wherein said biuret unit containing compound represents at least 10% by weight.
- A low viscosity polyfunctional isocyanate composition comprising at least one uretidinedione isocyanate dimer and at least one compound having a biuret function, wherein said biuret unit containing compound represents at least 20% by weight.
- 66. A composition comprising at least one compound of general formula X:



in which R' is a p-valent aliphatic group and p is an integer ranging from 0 to 5, and at least one compound of general formula II:

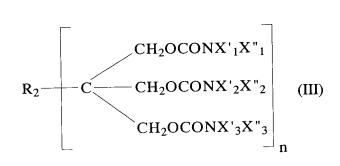


in which one or more of X_1 , X_2 and X_3 represents a group -R'-N=C=O as defined above and the others represent, where appropriate, a group

R' and p being as defined above,

and R_1 is R, with the OH groups substituted, where appropriate, with a group CONX $_1H$ wherein X_1 represents $R'(-N=C=O)_p$ group in which R' is as defined above, and n is an integer from 1 to 3;

and/or at least one compound of general formula III:



in which at least one of $NX'_1X''_1$, $NX'_2X''_2$ and $NX'_3X''_3$ represents the group

$$\begin{array}{c|c}
 & R' - (N = C = O)_p \\
\hline
 & -NH - R' - (N = C = O)
\end{array}$$

R' and p being as defined above, the others representing a group NX_1H with X_1 as defined above, and

 R_2 being R, with the OH groups substituted with a group CONX $_1\!H$ or

$$-CO = N = C = O)_p$$

$$C = NH = R' - (N = C = O)_p$$

$$O$$

as defined above,

and n is an integer ranging from 1 to 3,

and/or a biuret compound obtained from an isocyanate of general formula VI

$$-CO - N - (N - C - O)_{p}$$

$$C - NH - R' - (N - C - O)_{p}$$

$$0$$

$$(VI)$$

wherein R' and p are as defined above,

said composition further being free of dimerization catalyst of phosphine, aminopyridine, phosphoramide, organometallic or tertiary amine type.

67. A composition according to Claim 66, further comprising a compound of general formula VIII:

$$(O = C = N \xrightarrow{p} R' \xrightarrow{C} X' \xrightarrow{C} N = C = O)_{p}$$

$$(O = C = N \xrightarrow{p} R' \xrightarrow{C} X' \xrightarrow{C} N = C = O)_{p}$$

$$(VIII)$$

and/or a compound of general formula XIII:

$$O = C \xrightarrow{N} R' - (NCO)_{p}$$

$$(OCN)_{p} - R' - N \xrightarrow{C} NH - R' - (NCO)_{p}$$

$$O = C \xrightarrow{N} R' - (NCO)_{p}$$

wherein R" represents H or a hydrocarbon group.

68. A composition according to Claim 67 comprising at least one compound of general formula X and/or optionally one compound of general formula VIII and/or at least one compound of general formula XIII, said composition being free of dimerization catalysts.

A compound of general formula III

$$R_{2} = \begin{bmatrix} CH_{2}OCONX'_{1}X"_{1} \\ CH_{2}OCONX'_{2}X"_{2} \\ CH_{2}OCONX'_{3}X"_{3} \end{bmatrix}_{n}$$
(III)

in which

one or more of X_1 , X_2 and X_3 represents a group R'-(N=C=O)_p in which R' is a p-valent aliphatic group and p is an integer ranging from 0 to 5,

the others representing, where appropriate, a group of formula

R' and p being as defined above,

 R_1 is R, with the OH groups substituted, where appropriate, with a group CONX $_1H$, X_1 being as defined above,

at least one of NX'1X''1, NX'2X''2 and NX'3X''3 represents the group

$$\begin{array}{c}
R' - (N = C = O)_p \\
C - NH - R' - (N = C = O)_p \\
0
\end{array}$$
(V)

R' and p being as defined above, the others representing a group NX_1H or NX_1 -silyl with X_1 as defined above and R_2 being R, with the OH groups substituted, where appropriate, with a group $CONX_1H$, or

$$-CO - N - (N - C - O)_{p}$$

$$C - NH - R' - (N - C - O)_{p}$$

$$O - (VI)$$

R' and p being as defined above, and n is an integer ranging from 1 to 3,

in which at least one of the groups $NX'_1X''_1$, $NX'_2X''_2$ and $NX'_3X''_3$ represents the group of formula V as defined above, the others representing a group NX_1H with X_1 , $X'_1X''_1$, $X'_2X''_2$ and $X'_3X''_3$ as defined above and R^1 as defined above.

- 70. A compound according to Claim 69 in which:
- the groups $NX'_1X''_1$, $NX'_2X''_2$ and $NX'_3X''_3$ are selected from a group of general formula NX_1H , a group of general formula V, a uretidinedione group of formula V, an isocyanurate group of formula V.

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&$$

and, a biuret group of formula XII:

$$O = C \qquad R' \qquad \qquad (OCN)_p - R' - N \qquad NH - R' - (NCO)_p$$

$$O = C \qquad NH - R' - (NCO)_p$$

$$O = C \qquad NH - R' - (NCO)_p$$

R" represents H or a hydrocarbon-based group,

R₂ represents the group R with the OH groups substituted, where appropriate, with a group selected from CONHX₁, a group of formula VI, a group of formula XII) and -CO-NH- (group of formula XII), with the proviso that the compounds containing at least one carbamate group of formula NX₁H, or CONHX₁H respectively, and/or allophanate group of formula V, or -CO-NH- (group of formula V) respectively, and at least one group selected from a uretidinedione group of general formula IV, or -CO-NH- (group of general formula IV), respectively, an isocyanurate group of general formula XI, or -CO-NH- (group of general

formula XI) respectively, and a biuret group of general formula XII, or -CO-NH- (group of general formula XII) respectively.

- 71. A compound according to Claim 69, in which p is equal to 1 and containing 1, 2, 3 or 4 allopha (ate groups.
- 72. A compound according to Claim 69, wherein R' is a group selected from a group $(CH_2)_n$ with n ranging from 2 to 8, optionally substituted with a hydrocarbon-based chain optionally bearing an isocyanate function, a norbornylmethylene group, a cyclohexylmethylene group or a 3,3,5-trimethylcyclohexyl methylene group.
- 73. A composition for simultaneous or successive application, comprising:
 - at least one polyisocya ate composition according to Claim 65; and
 - a polyol.
- 74. A composition for simultaneous or successive application, comprising:
 - at least one polyisocyanate composition according to Claim 65; and
- a polyol of acrylate type which satisfies the following conditions for a dry extract (DE) of 75-80% by weight:
- Mw (weight-average molecular weight) not greater than 10,000, advantageously not greater than 5000;
 - Mn (number-average molecular weight) of not greater than 5000;
 - Mw/Mn (dispersity ratio) of not greater than 5;
 - number of OHs/molecule of greater than or equal to 2x
- 75. A composition for simultaneous or successive application, comprising:
 - at least one polyisocyanate composition according to Claim 65; and